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(54) Title: PEROXIDE-CROSSLINKABLE, LOW-HARDNESS, FLUORINE RUBBER COMPOSITION

(57) Abstract

Peroxide-vulcanizable fluoroelastomer compositions yield molded articles with a hardness of 50 or less.

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TITLE

PEROXIDE-CROSSLINKABLE, LOW-HARDNESS, FLUORINE RUBBER COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a novel vulcanization composition containing a fluoroelastomer. More specifically, the present invention is directed to a peroxide-vulcanizable fluoroelastomer composition which permits achievement of low hardness and excellent chemical resistance.

BACKGROUND OF THE INVENTION

Fluoroelastomers have excellent heat resistance and oil resistance. Therefore, they are used for O-rings, gaskets, oil seals, diaphragms, hoses, rolls, sheet materials, and the like in a variety of industrial fields, such as those involving automobiles, ships, aircraft, and hydraulic devices; the chemical industry and general appliances industry; and pollution-related fields.

Peroxide-vulcanizable fluoroelastomer products have exceptional acid and chemical resistance and are used for office equipment, in the fields of medical drugs and medical treatment, and in food product-related applications. Peroxide-vulcanized fluoroelastomer products having a low degree of hardness are desirable for applications which require acid or chemical resistance as well as good sealing properties with low tightening force in glass or plastic vessels. However, there are no examples of any such products which are satisfactory in terms of practical performance with a hardness of 50 or less.

There have been studies directed to lowering the hardness of peroxide-vulcanizable fluoroelastomers. In the method disclosed in Japanese Laid-Open Patent Application 62-277456, for example, a liquid fluorine rubber is blended in a solid fluorine rubber in a ratio of 100:10 to 100:100 to effect peroxide vulcanization so as to obtain a molded article having a hardness of 53 to 57. The addition of large amounts of the liquid fluorine rubber in this method, however, results in poor kneading workability, and it is still not possible to obtain a molded article with a hardness of 50 or less.

SUMMARY OF THE INVENTION

The present invention is a peroxide-vulcanizable fluoroelastomer composition which allows a molded article with a hardness of 50 or less to be obtained, which composition comprises

a) a peroxide-vulcanizable bromine-containing fluoroelastomer or iodine-containing fluoroelastomer, said fluoroelastomer having i) at least 20% by weight of a fraction having molecular weight of no more than 50,000, and ii) no more than 1% by weight of a fraction having molecular weight of 1,000,000 or more;

b) 0.1 to 5 parts by weight of an organic peroxide per 100 parts by weight of a); and

c) 0.1 to 5 parts by weight of a polyfunctional co-crosslinker per 100 parts by weight of a).

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a peroxide-vulcanizable fluoroelastomer composition which permits a molded article with a hardness of 50 or less to be obtained without impairing the kneading workability and without sacrificing the heat resistance, oil resistance, acid resistance, and chemical resistance which are characteristic of conventional peroxide-vulcanizable fluoroelastomers. It has been discovered that the aforementioned objectives can be achieved by provision of a composition obtained by blending a prescribed amount of an organic peroxide and a prescribed amount of a polyfunctional co-crosslinker with a peroxide-vulcanizable fluoroelastomer containing at least 20% by weight of a fraction having molecular weight of no more than 50,000 (hereinafter abbreviated as M50) and no greater than 1% by weight of a fraction having molecular weight of 1,000,000 or more (hereinafter abbreviated as M1000). It can thus be used in applications in the fields of office equipment, food products, medical drugs, and medical treatment instruments.

Examples of component a) of the present invention include binary copolymers having interpolymerized units of vinylidene fluoride (VDF) and hexafluoropropylene (HFP), or ternary copolymers having interpolymerized units of VDF, HFP, and tetrafluoroethylene (TFE),

either of which copolymers contain bromine and/or iodine in the polymer chain or polymer terminals. As used herein, "binary" and "ternary" refer to principal constituent monomers which do not include interpolymerized units of bromine-containing or iodine-containing monomers. Iodine or bromine is introduced into the polymer chain either by use of chain transfer agents or by copolymerization of bromine- or iodine-containing olefin monomers. Methods for manufacture of such polymers have been disclosed, for example, in Japanese Patent Application 59-7513.

Component b) of the present invention is an organic peroxide that produces peroxide radicals at the vulcanization temperature, for example, t-butyl cumyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di-(t-butylperoxy) hexane, and 2,5-dimethyl-2,5-2,5-di-(t-butylperoxy) hexane-3.

Component c) is a polyfunctional co-crosslinker. Examples of component c) of the present invention include triallylcyanurate, triallylisocyanurate, and trimethallylisocyanurate.

The ratio in which component b) is used is 0.1 to 5 parts by weight, and preferably 0.3 to 3 parts by weight, per 100 parts by weight of component a) of the present invention. Component c) is used in a ratio of 0.1 to 5 parts by weight, and preferably 0.3 to 3 parts by weight per 100 parts by weight of component a). Use of less than 0.1 weight part of component b) does not permit the necessary degree of crosslinking to be achieved, whereas an amount in excess of 5 parts by weight does not permit a hardness of 50 or less to be achieved. Use of less than 0.1 parts by weight of component c) does not allow the necessary degree of crosslinking to be achieved, whereas an amount in excess of 5 weight parts makes it difficult to achieve a hardness of 50 or less.

The molecular weight distribution of component a) is stipulated within the aforementioned range because less than 20% by weight of the M50 fraction does not allow a hardness of 50 or less to be achieved. Similarly, more than 1% by weight of the M1000 fraction also does not allow a hardness of 50 or less to be achieved.

Other components, such as carbon black, Austin black, graphite, silica, clay, diatomaceous earth, talc, calcium carbonate, calcium silicate, calcium sulfate, fatty acid calcium, fatty acid amides, low

molecular weight polyethylene, silicone oil, silicone grease, metal soap, stearic acid, fatty amines, titanium oxide, red iron oxide, and other such fillers, working adjuvants, plasticizers, coloring agents, and the like can be blended as needed into the fluoroelastomer composition of the present invention. Acid-absorbers, such as magnesium oxide, zinc oxide, calcium oxide, and calcium hydroxide, may also be added. One or two conventionally known vulcanization agents or vulcanization promoters may also be added, provided that the essence of the present invention is not thereby compromised.

Methods for vulcanizing the fluoroelastomer composition thus obtained include methods in which the material is kneaded using an open-type mixing roll or closed-type kneading roll (such as a Banbury mixer or a pressure kneader), and the material is then introduced into a heated mold and compressed to effect primary vulcanization, followed by secondary vulcanization. The conditions for the primary vulcanization include a temperature of 120° to 200°C, a time of 1 to 80 minutes, and a pressure of 20 to 150 kg/cm^2, and the conditions for the secondary vulcanization include a temperature of 120° to 250°C, and a time of 0 to 48 hours. Other vulcanization means which can be used include methods in which a preform is fashioned by injection or extrusion or the like, followed by vulcanization, or methods in which one or more ketones, ethers, or the like are used as media to prepare a solution or dispersion, which is then used to coat the surface of paper, fiber, film, sheets, plates, tubes, pipes, tanks, large-scale containers, or other molded articles, followed by vulcanization.

EXAMPLES

The present invention is described in further detail below with reference to certain preferred embodiments wherein all parts are by weight unless otherwise specified.

The molecular weight distribution of the fluoroelastomer and the physical properties, etc., of the vulcanized composition were determined using the following methods.

1) Molecular weight distribution:

Liquid chromatograph: model LC-3A (Shimadzu Seisakusho)

Columns: KF-80 M (two) & KF-800 P (precolumn) (Showa Denko)

Detector: ERC-7510 S (Elmer Optical)

Integrator: 7000 A (System Instruments)

Developing solvent: tetrahydrofuran

Polymer serving as standard for molecular weight detection lines: various types of monodisperse polystyrene (Toyo Soda)

Concentration: 0.1 wt%

Temperature: 35°C

(2) Physical properties of the vulcanized product:

Hardness measured according to JIS A.

100% tensile stress, tensile strength, elongation, and compression set measured according to JIS K 6301.

Example 1

Fluoroelastomer FR-6150 (100 parts by weight, 34% by weight M50 fraction and 0% M1000 fraction) manufactured by Asahi Chemical Industry (64.4 mol% VDF, 18.2 mol% HFP, 17.4 mol% TFE, 68.0 wt% F content, and 5200 ppm I content) was wound on an open-type mixing roll. Carbon black (3 parts by weight, Thermax N-990 from Cancarb), 1 part by weight lead oxide (Litharge No. 1 Canary Yellow from Nippon Chemical Industry), 0.5 part by weight 2,5-dimethyl-2,5-di (t-butylperoxy) hexane (Perhexa 2,5 B, from Nippon Oil & Fats), and 1 part by weight triallylisocyanurate (TAIC, from Nippon Chemical Industry) were kneaded and then allowed to age overnight.

The material was kneaded again, introduced into a mold, and press cured for 15 minutes at a temperature of 160°C for molded sheet or press cured for 20 minutes at a temperature of 160°C for molded JIS cylinder. The material was removed from the mold and heated for four hours in a circulating air oven at a temperature of 180°C to complete the secondary vulcanization, and the various tests were conducted. The results are shown in Table 1.

Example 2

Vulcanized molded material was prepared in the same manner as in Example 1 except that the amount of Perhexa 2,5 B used was 1 part by weight and the amount of TAIC used was 2 parts by weight. The various tests were conducted, and the results are shown in Table 1.

Example 3

Vulcanized molded material was prepared in the same manner as in Example 1 except that the amount of Perhexa 2,5 B used was 1.5 parts by weight and the amount of TAIC used was 3 parts by weight. The various tests were conducted, and the results are shown in Table 1.

Comparative Example 1

Vulcanized molded material was prepared in the same manner as in Example 1 except that the FR-6150 was replaced by FR-6350 (containing 13% M50 and 0% M1000) by Asahi Chemical Industry (64.4 mol% VDF, 18.2 mol % HFP, 17.4 mol % TFE, 68.0% F content, and 3000 ppm I content). The various tests were conducted. The results are shown in Table 1.

Comparative Example 2

Vulcanized molded material was prepared in the same manner as in Example 1 except that the FR-6150 was replaced by G-902 (containing 21% M50 and 1.5% M1000) by Daikin Industries (54.7 mol% VDF, 23.6 mol% HFP, 21.7 mol% TFE, 69.7% F content, and 2200 ppm I content). The various tests were conducted. The results are shown in Table 1.

Table 1. Summary of Formulations and Results

	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2
Blend					
Ex. 1 Polymer	100	100	100		
Comp. Ex. 1 Polymer				100	
Comp. Ex. 2 Polymer					100
Thermax N-990	3	3	3	3	3
Litharge No. 1 Yellow	1	1	1	1	1
TAIC	1	2	3	1	1
Perhexa 2,5 B	0.5	1	1.5	0.5	0.5
Vulcanizability @ 160°C					
Optimal time (min)	10.8	11.0	11.5	12.5	11.8
Physical Properties @ 23°C					
Hardness (points)	47	48	49	52	53
100% Tensile Stress (kgf/cm^2)	9	10	11	10	12
Tensile Strength (kgf/cm^2)	138	142	145	130	135
Elongation (%)	600	550	500	570	590
Compression Set					
25% compression, 150°C, 70 hr	28	23	20	33	30

CLAIMS:

1. A vulcanizable fluoroelastomer composition, which comprises

a) a peroxide-vulcanizable bromine-containing fluoroelastomer or iodine-containing fluoroelastomer, said fluoroelastomer having i) at least 20% by weight of a fraction having molecular weight of no more than 50,000 and ii) no more than 1% by weight of a fraction having molecular weight of 1,000,000 or more;

b) 0.1 to 5 parts by weight of an organic peroxide per 100 parts by weight of a); and

c) 0.1 to 5 parts by weight of a polyfunctional co-crosslinker per 100 parts by weight of a).

2. The vulcanizable fluoroelastomer composition of Claim 1, wherein the bromine-containing fluoroelastomer or iodine-containing fluoroelastomer is a binary copolymer having interpolymerized units of vinylidene fluoride and hexafluoropropylene.

3. The vulcanizable fluoroelastomer composition of Claim 1, wherein the bromine-containing fluoroelastomer or iodine-containing fluoroelastomer is a ternary copolymer having interpolymerized units of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene.

4. The vulcanizable fluoroelastomer composition of Claim 1, wherein component b) is present in an amount of 0.3 to 3 parts by weight.

5. The vulcanizable fluoroelastomer composition of Claim 1, wherein the amount of component c) is 0.3 to 3 parts by weight..

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/14093

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/00 //(C08K5/00,5:14,5:3492)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 600 090 (ASAHI KASEI KOGYO KK) 8 June 1994 see page 3, line 36 see page 4, line 6 see example 1 see claims 1-3,30,31,34,35	1,3-5
A	EP,A,0 340 786 (DU PONT DE NEMOURS & CO.) 8 November 1989 see page 5, line 14; examples; table 1 see claims 1,7,8	1-5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 94/14093

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0600090	08-06-94	US-A-	5374484	20-12-94
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